EPR and XRD as probes for activity and durability of LaMnO$_3$ perovskite-like catalysts

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Abstract

Four different LaMnO$_3$ perovskites were prepared by different procedures, characterised and tested for the catalytic flameless combustion of methane. EPR and XRD have been found useful probes for testing activity and durability of the catalysts, respectively. Broader EPR lines correspond to more active catalysts, while high crystallinity indicates long-lived samples. © 2000 Elsevier Science B.V. All rights reserved.

Many spinel-like, perovskite-like and other mixed-oxide samples show an EPR spectrum composed of a single Lorentzian-shaped line, as recently reviewed [1]. This simple spectroscopic feature has been attributed to paramagnetic ions interacting with each other. It has been also shown that systematic studies of these singlets, in particular of their line-width change vs. temperature and chemical composition, can provide interesting information on structure and on other physical characteristics related to the catalytic properties of the sample. Narrower EPR lines were observed, e.g. with Co$_3$O$_4$ samples calcined at higher temperatures. This was attributed to the presence of a lower concentration of structural defects [2], entraining a lower surface area [3] of the sample. Lorentzian-shaped EPR singlets were observed by us also with cobaltites [4,5], and narrower EPR lines were noticed with samples formed of smaller particles. EPR singlets have been observed also with cuprates [6] and with other mixed-oxides catalysts [7,8].

In this work we analysed four different perovskite samples of the same composition (LaMnO$_3$), but prepared by different procedures and we compared them as catalysts for the flameless combustion of methane. The aim was (i) to verify if a better durability was connected to a higher crystallinity, as indicated by XRD patterns and (ii) to highlight the correlation between width of the Lorentzian EPR line and catalytic activity.

Sample (a) was prepared by a recently reported procedure [9], involving the flame-hydrolysis of precursors at 1900 K for ca. 0.003 s. Sample (b) was prepared by the so-called citrate sol–gel method [10], followed by 3 h calcination at 873 K. Sample (c) was prepared by simply recalcining sample (b) for a further 3 h at 1023 K. The preparation procedure of sample (d) has been reported elsewhere [11]. Briefly, a solution of citric acid and ethylene glycol was added to a boiling solution of La and Mn nitrates, followed by evaporation under vigorous stirring to a viscous gel. The latter was then completely dried on a hot plate and then

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calcined at 1223 K for 23 h. The main characteristics of the samples are collected in Table 1.

EPR spectra have been collected by a Bruker ESP300 spectrometer. Catalytic activity was measured under standard reaction conditions, by means of a fixed-bed continuous quartz microreactor, by feeding a gaseous mixture of methane (0.5 vol%), oxygen (10 vol%) and nitrogen (balance) at GHSV = 12 000 h^{-1}, while increasing temperature by 10 K/min from 300 up to 873 K.

All the observed EPR lines were Lorentzian-shaped. Samples (a) and (b) showed only one broad line. Sample (d) showed an almost one order of magnitude narrower pattern only. Sample (c) showed a narrow Lorentzian-shaped line overlapping to a much broader feature. The room-temperature spectra are compared in Fig. 1. Only with samples (c) and (d) the line was temperature-broadened when $250 < T < 500$ K, as previously reported [11] for sample (d). By contrast, neither line-width nor line-shape-dependence on temperature was observed with the other two samples. XRD patterns (Fig. 2) showed that sample (a) was stoichiometric and orthorhombic [12], while samples (c) and (d) were rhombohedral [13]. Though undetectable by XRD, due either to low concentration or to low crystallinity, the orthorhombic phase could be present also in sample (c), generating the broad low-intensity EPR feature. Sample (b) was almost completely amorphous (Fig. 2(b)). Catalytic activity was expressed by the value of $T_{1/2}$, i.e., the temperature at which methane conversion attained 50% (Fig. 3).

More stable and durable catalysts possess a smaller amount n of structural defects. However, a lower value of n may be accompanied by a smaller surface area and, therefore, by a lower catalytic
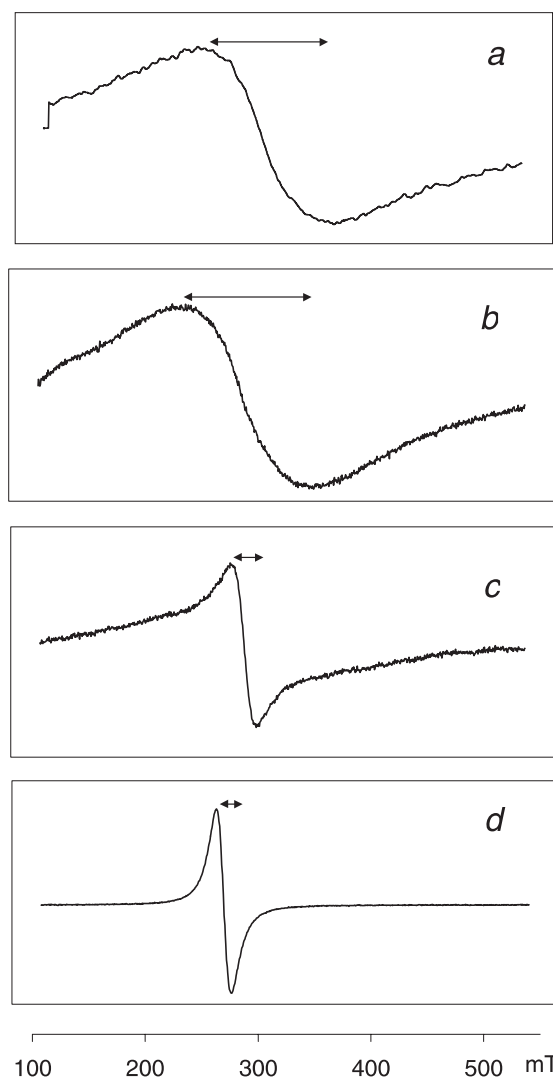

Fig. 1. (a)–(d): Room temperature EPR spectra of samples (a–d), respectively. Double arrows indicate ΔH_{pp} line-width (see Table 1).

activity. Furthermore, the *intrafacial* catalytic mechanism of methane combustion [14,15] requires abstraction of framework oxygen, which is favoured by a higher bulk oxygen mobility, connected with the presence of oxygen vacancies. Therefore, the number n of these vacancies is an important parameter for catalyst characterisation.

If, during calcination, the structural defects decrease following a first-order kinetics [2,3], one has
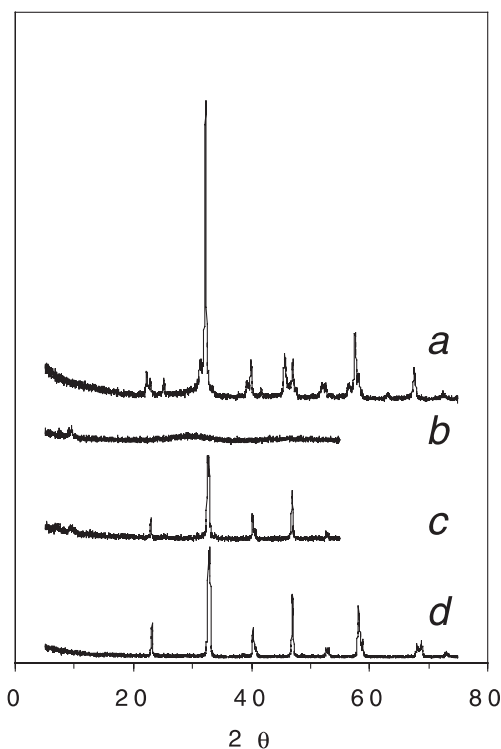
Table 1
Main characteristics of different LaMnO₃ samples

Sample	BET s.a. (m²/g)	T_p (K)	Calcin. time (s)	ΔH_{pp} [a] (G)
a	19.3	1900	3×10^{-3}	1122
b	46.1	873	1×10^4	1848
c	4.6	873–1023	1×10^4	450
d	4.2	1223	8×10^4	272

[a] At room temperature.

Fig. 2. XRD patterns of (a–d) samples (a–d) (Table 1), respectively. Relative intensity of the I_0 peak: (a) 3.5; (b) –; (c) 1; (d) 1.27.

Fig. 3. Catalytic activity expressed as temperature $T_{1/2}$ of 50% conversion, vs. EPR line-width ΔH_{pp}.

Fig. 4. Trend of k (Eq. (3)) vs. T_p.

$$\ln n(t) = \ln n_0 - kt, \tag{1}$$

where t is the duration of the calcination process and

$$k = A e^{-\Delta E^{\#}/k_B T_p}. \tag{2}$$

In Eq. (2), A is the Arrhenius pre-exponential factor, $\Delta E^{\#}$ the single-vacancy activation energy, i.e., the activation energy required to create a reticular oxygen by filling an oxygen vacancy with an oxygen atom, T_p the calcination (preparation) temperature and k_B is the Boltzmann's constant. Then, if $\Delta E^{\#} \ll k_B T_p$, the Taylor's expansion of Eq. (2) gives

$$k \cong A(1 - (\Delta E^{\#}/k_B T_p)). \tag{3}$$

Eqs. (1) and (3) indicate that $\ln nt$ decreases linearly with the duration t of the calcination process only, if the calcination temperature T_p is high enough, i.e., if $k_B T_p \gg \Delta E^{\#}$. However, the trend of k
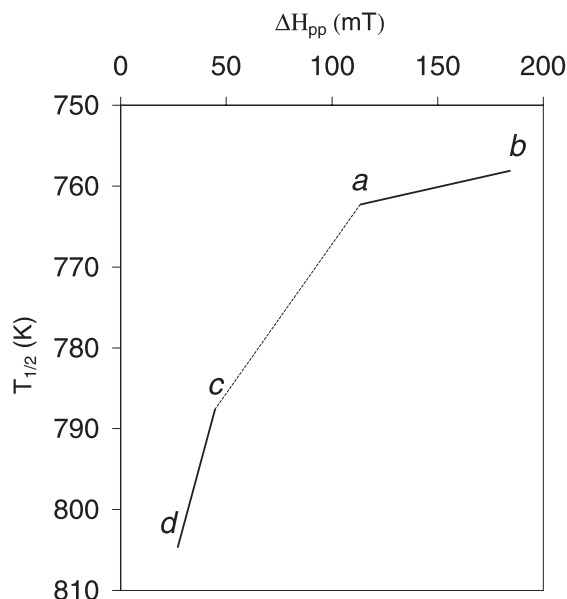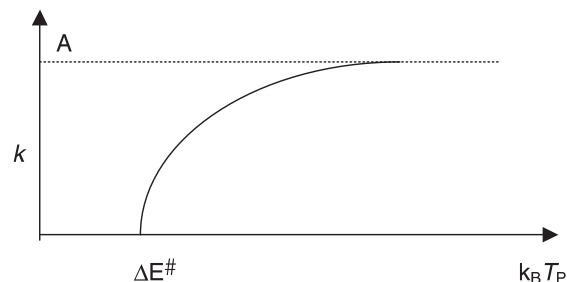
vs. $k_B T_p$, sketched in Fig. 4, shows that k becomes nearly equal to A at very high T_p values, i.e., when $\Delta E^{\#}$ becomes negligible with respect to $k_B T_p$. No further improvement of the calcination process efficiency is expected in this case by further increasing T_p. Therefore, the dependence of n on the combined effect of t and T_p is quite complex. In fact, a higher value of both t and T_p will favour a lower value of n, but in many cases the preparation procedure leads to an increased value of only one of them at a loss of the other. This could be the case of sample (a). Its preparation by flame-hydrolysis led to a very high value (1900 K) of T_p at a loss of t, which was ca. 3×10^{-3} s only. On the

other hand, its XRD pattern (Fig. 2(a)) fits almost exactly that of stoichiometric $LaMnO_3$ in orthorhombic phase [12]. Therefore, in this case, increasing temperature proved much more effective than increasing time in decreasing the value of n.

EPR analysis provides an independent information on the value of n. A rather complete theory of the different complex magnetic phenomena occurring in manganites has been reported elsewhere, supported by many experimental findings [11]. In this paper it was reported that the EPR line narrowed after catalytic use, due to a greater availability of Mn^{3+}. Indeed, the sample partially reduced during methane oxidation. Therefore, narrower lines, observer with aged catalysts, were related to greater amount of oxygen vacancies n.

In the present case, the Lorentzian-shaped EPR line is a bit broader with sample (b) than with (a) and the former showed a bit more active than the latter (Fig. 3), but by far less durable, because almost amorphous and so short-lived. Similarly, sample (c) was characterised both by a broader EPR line and by a higher catalytic activity than sample (d), though the latter possesses the same rhombohedral structure of the former. The EPR line-width is larger with sample (a) than with samples (c) and (d), due to a more distorted –Mn–O–Mn– bond angles in the orthorhombic than in rhombohedral structure [11,16]. This distortion could lead also to a higher oxygen availability in sample (a), accounting for its higher catalytic activity.

The conclusions one can draw from the present investigation are the following: (i) for a given composition, durable catalysts are characterised by highly crystalline structure; (ii) more active catalysts are characterised by higher-bulk oxygen mobility, related to higher concentration n of

structural defects. This leads to broader Lorentzian-shaped EPR line. Therefore, EPR line-width ΔH_{pp} is a reliable indicator of catalytic activity, while a good crystallinity characterises stable, long-lived catalysts.

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